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Abstract

In the present study a comparative evaluation of two methods for ^{137}Cs determination (pretreatment for gamma spectrometry) is attempted. One of them is the conventional AMP (ammonium molybdophosphate, $(NH_4)_3P(Mo_3O_{10})_4$) method (radiochemical treatment based on co – precipitation) and the other one is a method based on pre – concentration of cesium *in situ* by using the Mark III Centrifugal Pump. The pump, which is described analytically in the study, is composed of a motor (pump), four cartridge housings (containing the scavengers), a flow meter and a pressure tube (containing the battery pack and the timer board). For justification, this method is compared with the AMP co – precipitation one. Following up the radioanalytical procedures, the gamma spectrometry system (relative efficiency of high purity germanium detector 90%) is also demonstrated, as conformed to measuring obtained parameters. Finally, the advantages and disadvantages of these two methods are recorded and the application of each one is suggested.

1 Introduction

For the determination of ^{137}Cs the deep – sea *in situ* particle sampler named Mark III Centrifugal Pump, manufactured by Challenger Oceanic, is used [1]. The apparatus is considered as the "state of the art" on the issue (Figure 1). It is an appropriate tool as to provide sufficient quantities of samples for subsequent chemical analyses, even at a low concentration of conservative pollutants and dissolved ones scavenged on particles as well, encountered at mid – ocean depths. The Mark III sampler is designed to filter over one cubic meter of water in one hour. The volume sampled depends on the concentration of the suspended matter, the duration of pumping and the diameter, porosity and matrix of the filters used. The units are built for a safe working depth of 5500 m [1].
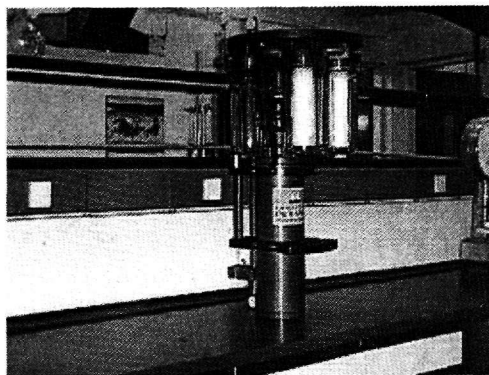
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Fig. 1. Mark III Centrifugal Pump

On the other hand the AMP method is described analytically. The last one is based on ion – exchange of radiocesium (^{137}Cs) with ammonium molybdophosphate $(NH_4)_3P(Mo_3O_{10})_4$. As a conventional method its great application is certificated.

2 Description of the two methods

2.1 Pre – concentration method

2.1.1 *Sampler description*

Common to all is the magnetically coupled centrifugal pump mounted on the end cap of a pressure tube. The pressure tube contains the motor, rechargeable or disposable battery packs, the relevant power supply (pcb) and the pre programmable timer board that controls the sampling. The volume sampled is monitored by a mechanical displacement flow meter. The following Figure (Figure 2) shows the Mark III units analytically [1].

The following table gives the specification of the used pump and the absolute description of its units.

2.1.2 *Filter preparation – Impregnation*

Various transition metal ferrocyanides for collecting, both by precipitating and *in situ* adsorbing, radiocesium from sea water have been used for about 30 years [2,6,13]. The advantages of using transition metal ferrocyanides are that they, due to their gelatinous form, can be easily attached to the supporting material. The exchange capacity of some transition metal ferrocyanides is

PREFILTER SECTION

CARTRIDGE HOUSINGS

CARTRIDGES

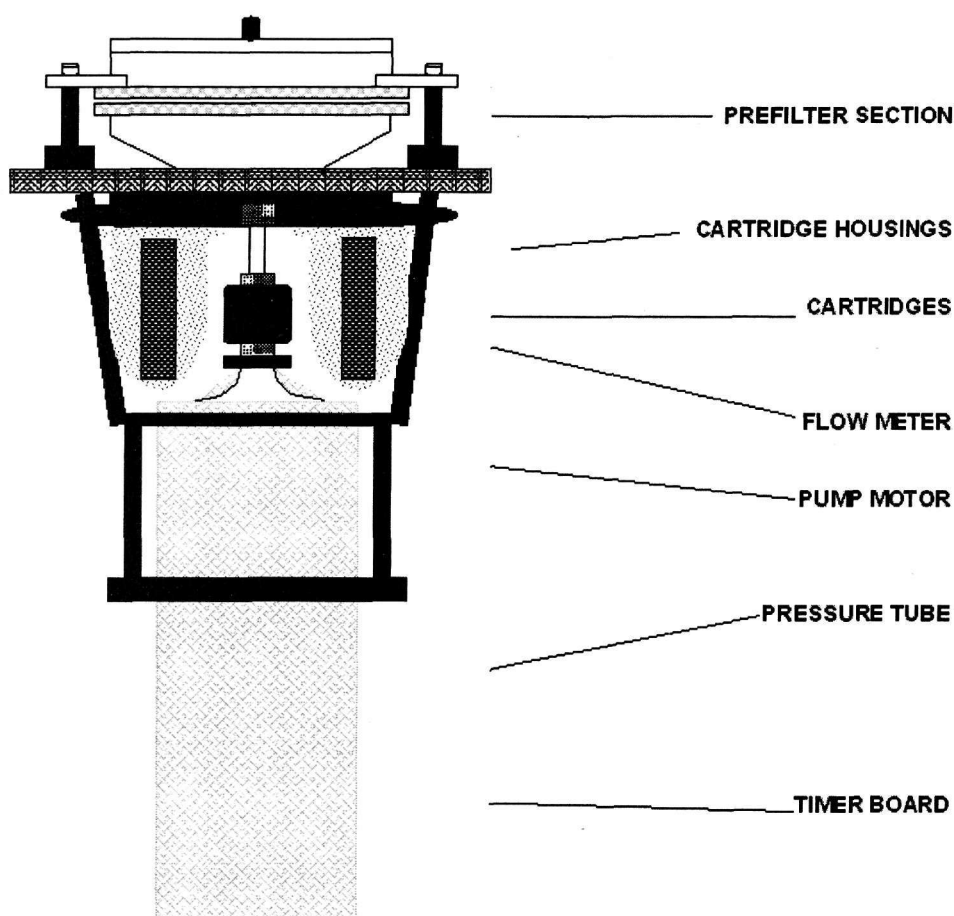FLOW METER

PUMP MOTOR

PRESSURE TUBE

TIMER BOARD

Fig. 2. Main Units of Mark III Centrifugal Pump

extremely great and it is also easy to be manufactured by the scientists in the laboratory due to the low cost reagents included [2,10,11,12].

The types of ferrocyanides used as inorganic ion – exchangers for cesium include copper ferrocyanide [2,6], zirconium ferrocyanide [2] and potassium hexacyanocobalt [4]. The first two mentioned are generally to be preferred due to their higher mechanical stability and far lower potassium content. High mechanical stability is very important in order not to lose any adsorbent when exposing it to sea water [2]. In the present work we use copper ferrocyanide $Cu_2[Fe(CN)_6]$ as ion – exchanger, impregnated of cotton wound cartridge filters [2].

The filter impregnation is achieved using copper ferrocyanide solution in several concentrations (2.5, 5.0, 7.5 mM). The aim is to determine the best concentration of $Cu_2[Fe(CN)_6]$, which succeeds the maximum exchange efficiency

Table 1
Specification of Mark III Centrifugal Pump

Pressure tube	Hard anodized Al alloy pressure tube containing batteries and electronics
Pump head and drive	Centrifugal pump with ceramic bearings, magnetically coupled to a printed armature motor
Filter housings	293 mm diameter polypropylene housings
Prefilter	Not included
Cartridge filters	4 filter housings. The first filter as prefilter, the next 2 scavengers, the fourth empty. For radionuclides, Nuclepore 1 or 0.4 mm porosity cartridges impregnated with copper Ferrocyanide for soluble ^{137}Cs.
Battery packs	2x16 V, 5 A rechargeable lead – acid battery packs or non – rechargeable alkaline or lithium – manganese dioxide packs.
Timer Control	Magnetically activated lapsed time timer, up to 999.9 hr delay, 9.9 hr pumping
Volume meter	Mechanical displacement flow meter, accurate to $\pm$ 2%; flow rates of 100-300 L/min
Deployment	Ship's wire to full ocean depth; using a conductive cable; moorings
Dimensions	1000 mm high (max) x 400 mm wide x 500 mm deep
Weight in air	40 kg depended on configuration
Weight in water	20 kg depended on configuration
Sample – Volume	Approximately 1000 l/hr at mid – ocean depths depended on filter types
Rated depth	To 5500 m

of ^{137}Cs [2]. The derivation reaction is demonstrated as follows:

$$K_4[Fe(CN)_6] + 2\ Cu(NO_3)_2\ Cu_2[Fe(CN)_6] + 4\ KNO_3$$
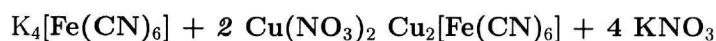
Impregnation of the filters is performed by circulating the necessary amounts of water, $K_4[Fe(CN)_6]$ and $Cu(NO_3)_2$ in a closed loop, which includes a small pump and the filter to be impregnated [5,10]. The filter collects the reddish – brown precipitate formed. When the circulating solution is clear, the impregnated filter is dried in an oven at 60 – 80 ^{o}C for due time, making it ready for use [2].

2.1.3 *Mark III preparation*

This process should be reached two months before the cruise. We check the pump heads to make sure they are free of salt. We also put Vaseline on the filter housings and all holding screws; we check the battery condition, the pcb and the motor by running the test cycle [1].

2.1.4 *In situ sampling*

A test cycle should be carried out before setting the true delay and sampling time in order to check the pump condition. During the test procedures, with the TEST toggle switch held on, each tenth of a unit equals 1 second and each whole unit 10 seconds. We set the times with a small screwdriver selecting a "delay" time of 1.5 and a "pump" time 0.5 (15 sec and 5 sec). We connect the battery to the board and the LCD will light up. We pass the magnet over the STOP switch to reset the pump latch. Then we push the SET switch on the right hand side and the times preset appears on the LCD. We hold the magnet under the START and after 3 seconds the speaker will squeak; the timer sequence has started. Finally, we push the TEST toggle switch on the left and hold it on. There is 15 seconds delay, before the pump runs on for 5 seconds and then the motor ramps down [1]. The next figure shows the timer board of a Mark III sampler, which is located inside the pressure tube, the LCD and each toggle used.
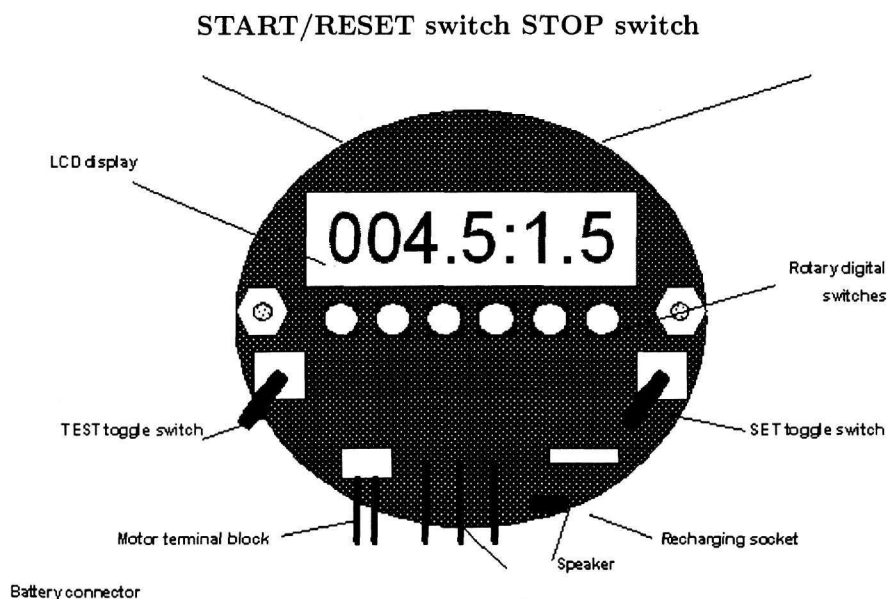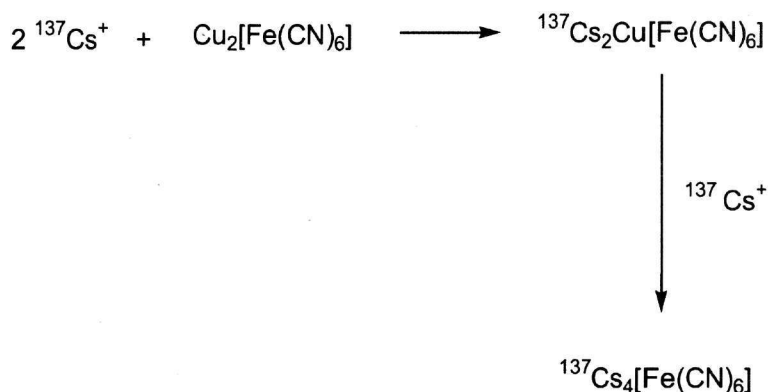
START/RESET switch STOP switch

Fig. 3. The timer board

We mark the initial rate from the flow meter in order to known the true volume of the water sampled. To set the true cast time we clear the latch by passing the magnet over the "STOP" switch. Afterwards, we set the delay and the sampling time and push the "SET" toggle to load the time set to the display. The timing sequence begins when the magnet is held over the "START" switch for 3 seconds [1].

2.1.5 *Laboratory work*

After reaching the very important processes of post deployment and maintenance of Mark III sampler, having large volume filtration, each filter is dried and ashed at 420 ^{o}C for 48 h. The ash is carefully collected and analysed by gamma spectrometry [7]. Assuming the two impregnated filters have the same collection efficiency and thus adsorb the same fraction of radiocesium reaching them, one may calculate the amount of dissolved radiocesium A(^{137}Cs), in the water volume sampled by considering the two filters to be the two first terms in a geometrical series, which has a sum of A(^{137}Cs) = A_1 / (1-A_2/A_1), where A_1 and A_2 are the radiocesium activities on the first and the second impregnated filters, respectively [2].

The ion – exchange reaction of ^{137}Cs can be seen below:

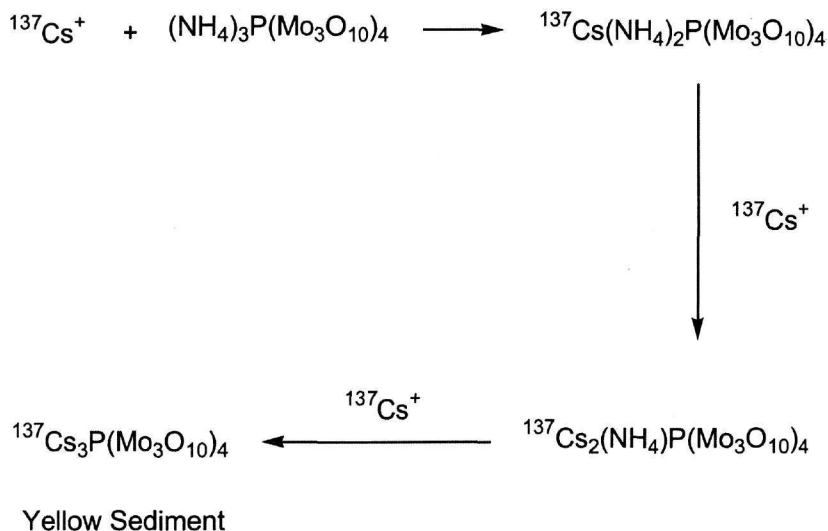$$2\ ^{137}Cs^+\ +\ Cu_2[Fe(CN)_6]\ \longrightarrow\ ^{137}Cs_2Cu[Fe(CN)_6]$$

$$\Big\downarrow\ ^{137}Cs^+$$

$$^{137}Cs_4[Fe(CN)_6]$$

2.2 AMP method

In this method ion – exchange of cesium with AMP ($(NH_4)_3P(Mo_3O_{10})_4$) takes place and a yellow sediment is precipitated. This one is analysed by gamma spectrometry. The disadvantage of this method consists in transportation of high volumes of sea water samples in the laboratory [16,17]. Specifically, samples of 60 – 100 l of sea water are collected in plastic vessels, previously rinsed sequentially by distilled water and 10% HNO_3. Directly, samples are acidified to pH 2.0 – 2.5 by 65% HNO_3 and 0.2 Bq/l ^{134}Cs (tracer) are added. The sample is transferred in the laboratory and addition of 65% HNO_3 to pH 1.5 and

400 mg/l micro – crystalline AMP is followed and the mixture is stirred for 15 minutes. The sediment is precipitated for 16 – 48 hours and the supernatant solution is spilled (a low volume remains just to wet the sediment). The sediment is transferred in a 2 l beaker by flushing it with 0.05 N HNO_3 and leaved for precipitation. Then the sediment is filtered, transferred in a measurement pot and dried in 60 ^oC for 10 minutes. Finally, the measurement pot is covered by a transparent plexiglas matter and analyzed by gamma spectrometry. The determination ends considering the ^{134}Cs mass added [17,18].

The ion – exchange reaction of ^{137}Cs can be seen below:

$$^{137}Cs^+ \;+\; (NH_4)_3P(Mo_3O_{10})_4 \longrightarrow {}^{137}Cs(NH_4)_2P(Mo_3O_{10})_4$$

$$\downarrow {}^{137}Cs^+$$

$$^{137}Cs_3P(Mo_3O_{10})_4 \xleftarrow{\;{}^{137}Cs^+\;} {}^{137}Cs_2(NH_4)P(Mo_3O_{10})_4$$

Yellow Sediment

2.3 Gamma spectrometry

The measurement pot is of 68 mm height and 200 mm diameter with a transparent plexiglas cover of 4 mm thickness. The pot is adapted on the Germanium detector [14,19]. The measurement duration is about 70000 seconds, usually overnight, depending on the sample type.

A high resolution gamma spectrometry system is used. The system consists of a high purity Germanium detector (CANBERRA Coaxial Ge Detector Systems) with 90% relative efficiency and 2.1 keV resolution (Full Width at Half Maximum) at 1.33 MeV (photopeak ^{60}Co) [15,19]. The HpGe detector is connected with a 16000 – channel analyzer (CANBERRA Genie 2000) [15,20]. The whole system is controlled by special software (CANBERRA Genie 2000). The energy calibration is performed periodically using standard sources (^{22}Na,
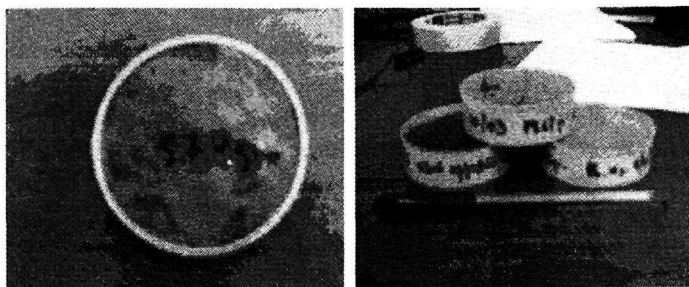
Fig. 4. The measurement pot

[54]Mn, [57]Co, ^{60}Co, [109]Cd, [133]Ba, ^{137}Cs, [241]Am) [15,19]. Energy calibration is performed by using a certificate file of the software [22]. The last one allows selecting the calibration file defining the list of energy/channel pairs to be used for calibration [22]. The detector's resolution (Full Width at Half Maximum) is checked periodically in the 1.33 MeV (photopeak ^{60}Co) [19,14]. The detector's efficiency is calculated in each energy by using standard active source of [226]Ra, in equilibrium with [222]Rn and each decay products, in the same geometry with the measurement pot. The standard sources' activity is 240 Bq [19,14]. The low limit detection (L.L.D.) of ^{137}Cs for the pre-concentration method is 0.05 Bq/m^3. Thus, the low limit detection for the AMP co-precipitation method is 0.04 Bq/m^3.

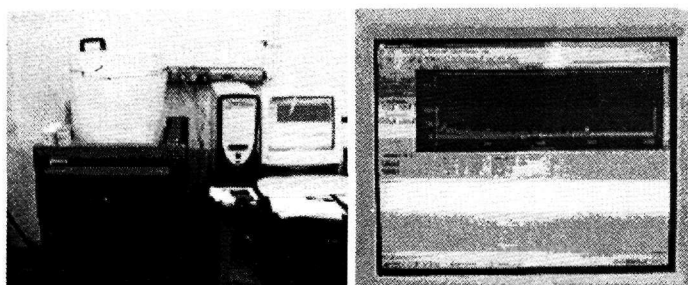Fig. 5. The HpGe detector and its software

3   Results and conclusions

Comparing the two methods described above some comments can be extracted as regards of the advantages and the disadvantages of each one, e.g.:

3.1 *Pre – concentration method*

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Advantages

¬It is an _in situ_ pre – concentration method, large volumes sample are treated in field. Therefore, there is no need for large volume samples to be transferred to the laboratory.

¬Simple and short treatment of samples in the laboratory is performed.

Disadvantages

¬ 10– 20% lower yield compared to the AMP one because of the expected loss of material during ashing procedure is supplied.

¬The pump can be used by experienced personnel.

¬It is expensive method, because of the instrumentation and expendables used (pump, filters, batteries, filters).

3.2 _AMP method_

Advantages

¬The method can be used by any technician in chemistry.

¬There is no need for high experienced persons for sampling.

Disadvantages

¬Large volume samples should be transferred in the laboratory (60 – 100 l at least) for analysis.

Final conclusion: The pre – concentration method can be used for monitoring the environmental radioactivity easily (if qualification of persons involved is achieved). On the other hand, AMP method as a conventional one is easily applicable. Finally, both methods are recommended for emergency situations (radiological events), each one selected on case.

4. Acknowledgements

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